CLAIMS

1. A process for producing oxygenated products from a Fischer-Tropsch derived olefinic feedstock, which process includes reacting the feedstock, in a hydroformylation reaction stage, with carbon monoxide and hydrogen at an elevated reaction temperature and at a superatmospheric reaction pressure in the presence of a hydroformylation catalyst system, which comprises a mixture, combination or complex of

(i) a transition metal, T, where T is selected from the transition metals of Group VIII of the Periodic Table of Elements;

(ii) carbon monoxide, CO;

(iii) hydrogen, H_2;

(iv) as a primary ligand, a monodentate phosphorus ligand; and

(v) as a secondary ligand, a bidentate phosphorus ligand which confers resistance on the catalyst system to poisoning arising from the presence of undesired components in the Fischer-Tropsch derived feedstock.

2. A process according to Claim 1, wherein T is Co, Ir, Pd or Rh.

3. A process according to Claim 2, wherein T is Rh, with compound (i) being selected from $Rh(acac)(CO)_2$ where 'acac' is acetylacetonate; Rh(acac)(CO)(TPP) where 'acac' is acetylacetonate and 'TPP' is triphenylphosphine; $[Rh(OAc)_2]_2$ where 'OAc' is acetate; Rh_2O_3; $Rh_4(CO)_{12}$; $Rh_6(CO)_{16}$; $Rh(CO)_2$(dipivaloyl methanoate); and $Rh(NO_3)_2$.

4. A process according to Claim 2, wherein the hydroformylation reaction stage comprises a hydroformylation reactor, with the process including initially preparing the catalyst system by dissolving component (i), together with the ligands, in a solvent, to produce a catalyst solution, and heating the catalyst

solution in the reactor in the presence of synthesis gas comprising CO and H_2 to form an active hydroformylation catalyst system in which the rhodium concentration in the catalyst solution in the hydroformylation reactor is from 10 to 1000 ppm.

5. A process according to Claim 3 or Claim 4, wherein the monodentate phosphorus ligand is used in a molar excess, relative to the rhodium, of from 50:1 to 1000:1.

6. A process according to any one of Claims 3 to 5 inclusive, wherein the bidentate phosphorus ligand is employed at a lower ligand to rhodium molar ratio than the monodentate phosphorus ligand, and wherein the bidentate phosphorus ligand to rhodium ratio is from 0.2:1 to 100:1.

7. A process according to any one of Claims 1 to 6 inclusive, wherein the monodentate phosphorus ligand is

$P(R^a)(R^a)(R^a)$ (L1a)

where all R^a are the same or are dissimilar, and are each a branched or straight chain alkyl or aryl radical.

8. A process according to Claim 7 wherein, in the ligand of formula (L1a), each R^a is an aryl group and all R^a are the same.

9. A process according to Claim 8 wherein, in the ligand of formula (L1a), each R^a is phenyl so that ligand (L1a) is triphenylphosphine.

10 A process according to any one of Claims 1 to 6 inclusive, wherein the monodentate phosphorus ligand is

$P(OR^a)(OR^a)(OR^a)$ (L1b)

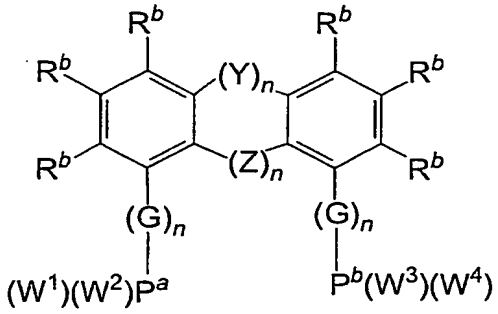
where all R^a are the same or are dissimilar, and are each a branched or straight chain alkyl or aryl radical.

11 A process according to Claim 10 wherein, in the ligand of formula (L1b), each R^a is an aryl group and all R^a are the same.

12. A process according to Claim 11 wherein, in the ligand of formula (L1b), each R^a is a substituted phenyl ring.

13. A process according to Claim 12, wherein the ligand (L1b) is tris(2,4-ditertiary butylphenyl) phosphite or tris(2-tertiary butylphenyl) phosphite.

14. A process according to any one of Claims 1 to 13 inclusive, wherein the bidentate phosphorus ligand is



(L2a)

wherein

(i) all R^b are the same or are dissimilar, and are each H, alkyl, alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl, aryloxy, polyether, cyano, nitro, halogen, trifluoromethyl, $-C(O)R^c$, $-(R^d)C(O)R^c$, $-CHO$, $(R^d)CHO$, $-COOR^c$, $-(R^d)COOR^c$, $-COO^-M^+$, $-(R^d)COO^-M^+$, $-SO_3R^c$, $-(R^d)SO_3R^c$, $-SO_3^-M^+$, $-(R^d)SO_3^-M^+$, $-SR^c$, $-(R^d)SR^c$, $-SOR^c$, $-R^d(SOR^c)$, $-NR^c$, $-(R^d)NR^c$, $-N^+(R^c)(R^c)(X^-)$ or $-(R^d)N^+(R^c)(R^c)(X^-)$, wherein

(a) R^c and R^d are the same or different, and are each H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical;

(b) M^+ is a cation; and

(c) X^- is an anion;

(ii) Y and Z are independent bridges, are the same or different, and are each selected from the radicals $-O-$, $-N(R^c)-$, $-N^+(R^c)(R^c)(X^-)-$, $-N(C(O)R^c)-$, $-C(R^c)(R^c)-$, $-C(C(R^c)(R^c))-$, $-C(O)-$, $-S-$, $-Si(R^c)(R^c)-$, $-Si(OR^c)(OR^c)-$, $-P(R^c)-$ or $-P(OR^c)-$, where R^c and X^- are as hereinbefore defined;

(iii) n (in $(Y)_n$ and $(Z)_n$) is, in each case, 0 or 1, with the proviso that n cannot be 0 for both Y and Z;

(iv) W^1, W^2, W^3 and W^4 are the same or different, and are each an alkyl (branched or straight chain), alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl, aryloxy or trifluoromethyl radical;

(v) a, b, in P^a and P^b, are used merely to identify the P atoms;

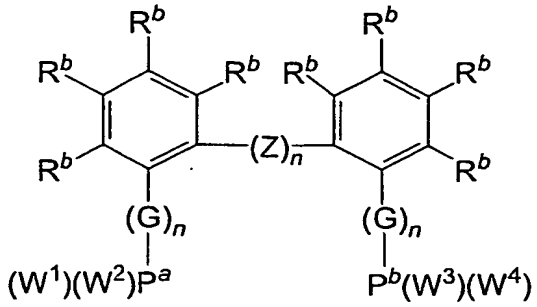
(vi) each G is an independent linker radical, are the same or different, and is selected from $-O-$, $-N(R^f)-$, $-N^+(R^f)(R^f)(X^-)-$, $-C(R^f)(R^f)-$, $-S-$, $-Si(R^f)(R^f)-$, $-C(F_2)-$ or $-C(R^f)(F)-$, wherein

(c) R^f is H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical, and with the proviso that when the radical contains more than one R^f, all R^f are the same or different;

(d) X^- is as defined above; and

(vii) n (in each $(G)_n$) is 0 or 1.

15. A process according to any one of Claims 1 to 13 inclusive, wherein the bidentate phosphorus ligand is



(L2b)

wherein

(i) all R^b are the same or are dissimilar, and are each H, alkyl, alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl, aryloxy, polyether, cyano, nitro, halogen, trifluoromethyl, $-C(O)R^c$, $-(R^d)C(O)R^c$, $-CHO$, $(R^d)CHO$, $-COOR^c$, $-(R^d)COOR^c$, $-COO^-M^+$, $-(R^d)COO^-M^+$, $-SO_3R^c$, $-(R^d)SO_3R^c$, $-SO_3^-M^+$, $-(R^d)SO_3^-M^+$, $-SR^c$, $-(R^d)SR^c$, $-SOR^c$, $-R^d(SOR^c)$, $-NR^c$, $-(R^d)NR^c$, $-N^+(R^c)(R^c)(X^-)$ or $-(R^d)N^+(R^c)(R^c)(X^-)$, wherein

(a) R^c and R^d are the same or different, and are each H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical;

(b) M^+ is a cation; and

(c) X^- is an anion;

(ii) Z is an independent bridge, and is selected from the radicals $-O-$, $-N(R^c)-$, $-N^+(R^c)(R^c)(X^-)-$, $-N(C(O)R^c)-$, $-C(R^c)(R^c)-$, $-C(C(R^c)(R^c))-$, $-C(O)-$, $-S-$, $-Si(R^c)(R^c)-$, $-Si(OR^c)(OR^c)-$, $-P(R^c)-$ or $-P(OR^c)-$, where R^c and X^- are as defined above;

(iii) n (in $(Z)_n$) is 1;

(iv) W^1, W^2, W^3 and W^4 are the same or different, and are each an alkyl (branched or straight chain), alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl, aryloxy or trifluoromethyl radical;

(v) a, b, in P^a and P^b, are used merely to identify the P atoms;

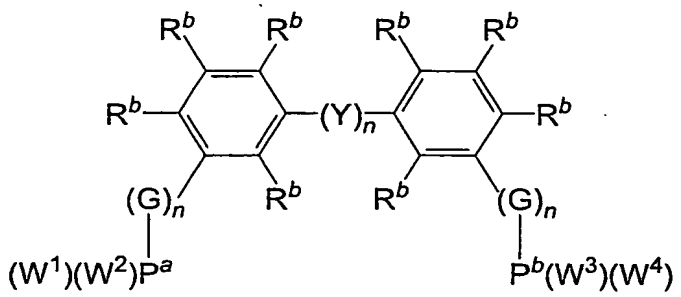
(vi) each G is an independent linker radical, are the same or different, and is selected from $-O-$, $-N(R^f)-$, $-N^+(R^f)(R^f)(X^-)-$, $-C(R^f)(R^f)-$, $-S-$, $-Si(R^f)(R^f)-$, $-C(F_2)-$ or $-C(R^f)(F)-$, wherein

(e) R^f is H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical, and with the proviso that when the radical contains more than one R^f, all R^f are the same or different;

(f) X^- is as defined above; and

(vii) n (in each $(G)_n$) is 0 or 1.

16. A process according to any one of Claims 1 to 13 inclusive, wherein the bidentate phosphorus ligand is



(L2c)

wherein

(i) all R^b are the same or are dissimilar, and are each H, alkyl, alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl, aryloxy, polyether, cyano, nitro, halogen, trifluoromethyl, $-C(O)R^c$, $-(R^d)C(O)R^c$, $-CHO$, $(R^d)CHO$, $-COOR^c$, $-(R^d)COOR^c$, $-COO^-M^+$, $-(R^d)COO^-M^+$, $-SO_3R^c$, $-(R^d)SO_3R^c$, $-SO_3^-M^+$, $-(R^d)SO_3^-M^+$, $-SR^c$, $-(R^d)SR^c$, $-SOR^c$, $-R^d(SOR^c)$, $-NR^c$, $-(R^d)NR^c$, $-N^+(R^c)(R^c)(X^-)$ or $-(R^d)N^+(R^c)(R^c)(X^-)$, wherein

(a) R^c and R^d are the same or different, and are each H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical;

(b) M^+ is a cation; and

(c) X^- is an anion;

(ii) Y is an independent bridge, and is selected from the radicals $-O-$, $-N(R^c)-$, $-N^+(R^c)(R^c)(X^-)-$, $-N(C(O)R^c)-$, $-C(R^c)(R^c)-$, $-C(C(R^c)(R^c))-$, $-C(O)-$, $-S-$, $-Si(R^c)(R^c)-$, $-Si(OR^c)(OR^c)-$, $-P(R^c)-$ or $-P(OR^c)-$, where R^c and X^- are as hereinbefore defined;

(iii) n (in $(Y)_n$) is 1;

(iv) W^1, W^2, W^3 and W^4 are the same or different, and are each an alkyl (branched or straight chain), alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl, aryloxy or trifluoromethyl radical;

(v) a, b, in P^a and P^b, are used merely to identify the P atoms;

(vi) each G is an independent linker radical, are the same or different, and is selected from $-O-$, $-N(R^f)-$, $-N^+(R^f)(R^f)(X^-)-$, $-C(R^f)(R^f)-$, $-S-$, $-Si(R^f)(R^f)-$, $-C(F_2)-$ or $-C(R^f)(F)-$, wherein

(g) R^f is H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical, and with the proviso that when the radical contains more than one R^f, all R^f are the same or different;

(h) X^- is as defined above; and

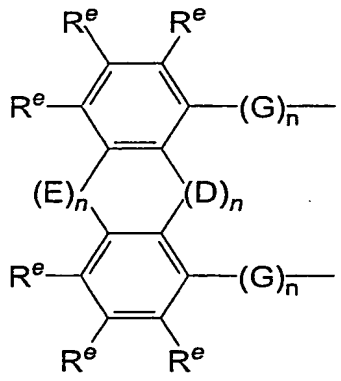
(vii) n (in each $(G)_n$) is 0 or 1.

17. A process according to any one of Claims 14 to 16 inclusive wherein, in the ligand (L2a), (L2b) or (L2c), M^+ is an ion of an alkali or alkali earth metal, or is ammonium or a quaternary ammonium ion.

18. A process according to any one of Claims 14 to 17 inclusive, wherein, in the ligand (L2a), (L2b) or (L2c), X^- is an organic acid, phosphate or sulphate group.

19. A process according to any one of Claims 14 to 18 inclusive wherein, in the ligand (L2a), (L2b) or (L2c), W^1, W^2, W^3 and W^4 are each an alkyl, aryl or aryloxy radical.

20. A process according to Claim 19 wherein, in the ligand (L2a), (L2b) or (L2c), W^1, W^2, W^3 and W^4 are each an aryl or aryloxy radical in accordance with formula (1), with the proviso that the structure of formula (1) does not represent a bridging unit connecting P^a to P^b – for P^a, W^1 and W^2 represent radicals connected through their respective G linkers, and for P^b, W^3 and W^4 represent radicals connected through their respective G linkers



(1)

wherein

(i) all R^e are the same or are different, and are each H, alkyl, alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl, aryloxy, polyether, cyano, nitro, halogen, trifluoromethyl, $-C(O)R^c$, $-(R^d)C(O)R^c$, $-CHO$, $(R^d)CHO$, $-COOR^c$, $-(R^d)COOR^c$, $-COO^-M^+$, $-(R^d)COO^-M^+$, $-SO_3R^c$, $-(R^d)SO_3R^c$, $-SO_3^-M^+$, $-(R^d)SO_3^-M^+$, $-SR^c$, $-(R^d)SR^c$, $-SOR^c$, $-R^d(SOR^c)$, $-NR^c$, $-(R^d)NR^c$, $-N^+(R^c)(R^c)(X^-)$ or $-(R^d)N^+(R^c)(R^c)(X^-)$, wherein

(a) R^c and R^d are the same or different, and are each H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical;

(b) M^+ is a cation; and

(c) X^- is an anion;

(ii) each G is an independent linker radical, are the same or different, and is selected from $-O-$, $-N(R^f)-$, $-N^+(R^f)(R^f)(X^-)-$, $-C(R^f)(R^f)-$, $-S-$, $-Si(R^f)(R^f)-$, $-C(F_2)-$ or $-C(R^f)(F)-$, wherein

(d) R^f is H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical, and with the proviso that when the radical contains more than one R^f, all R^f are the same or different;

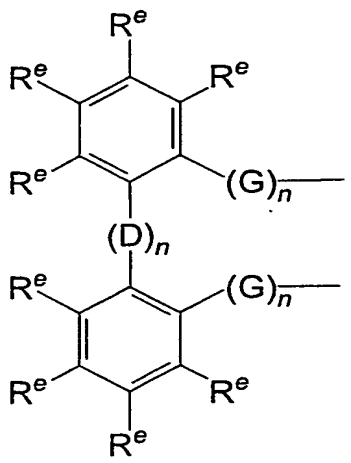
(e) X^- is as defined above; and

(iii) n (in each $(G)_n$) is 0 or 1;

(iv) D and E are each an independent bridge, are the same or different, and are each selected from the radical, $-O-$, $-N(R^c)-$, $-N^+(R^c)(R^c)(X^-)$, $-N(C(O)R^c)-$, $-N(SiR_2^c)-$, $-C(R^c)(R^c)-$, $-C(C(R^c)(R^c))-$; $-C(O)-$, $-S-$, $-Si(R^c)(R^c)-$, $-Si(OR^c)(OR^c)-$, $-P(R^c)-$ or $-P(OR^c)-$, wherein R^c is H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical, and X^- is as defined above;

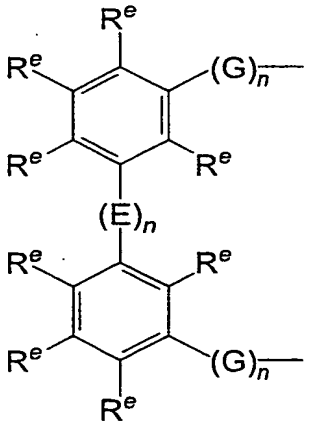
(v) n (in each of (D)n and (E)n) is 0 or 1.

21. A process according to Claim 20 wherein, in formula (1), n=0, in $(E)_n$, so that the independent E bridge is absent; formula (1) will then have the structure of formula (2)



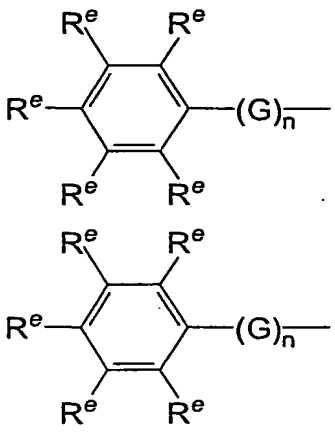
(2)

22. A process according to Claim 20 wherein, in formula (1), n=0, in (D)n, so that the independent D bridging is absent; formula (1) will then have the structure of formula (3)



(3)

23. A process according to Claim 20 wherein, in formula (1), n=0, in both (D)n and (E)n, so that both the independent bridges D and E are absent; formula (1) will then have the structure of formula (4)



(4)

24. A process according to any one of Claims 1 to 13 inclusive, wherein the bidentate phosphorus ligand is

$$(W^1)(W^2)P^a—(G)_n—(A)—(G)_n—P^b(W^3)(W^4)$$

(L2d)

wherein

(i) each G is an independent linker radical, are the same or different, and is selected from $-O-$, $-N(R^f)-$, $-N^+(R^f)(R^f)(X^-)-$, $-C(R^f)(R^f)-$, $-S-$, $-Si(R^f)(R^f)-$, $-C(F_2)-$ or $-C(R^f)(F)-$, wherein

(a) R^f is H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical, and with the proviso that when the radical contains more than one R^f, all R^f are the same or different;

(b) X^- is an anion; and

(ii) n (in each $(G)_n$) is 0 or 1;

(iii) a, b, in P^a and P^b, are used merely to identify the P atoms;

(iv) W^1, W^2, W^3 and W^4 are the same or different, and are each an alkyl (branched or straight chain), alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl, aryloxy or trifluoromethyl radical; and

(v) A is a bridging unit and is selected from one of the following diradicals: $-(CR^b_2)_n-$, $-(CR^b)_n-$, $-(CR^bCR^b)_n-$, $-[C(O)]_n-$, $-[C(O)C(R^b)_2]_n-$, $-(NR^b)_n-$, $-S-$, $-(SiR^b_2)_n-$, $-(SiOR^b_2)_n-$, with

(c) any alkyl radical having n = 1 to 5 and being cyclic, straight or branched or straight;

(d) R^b being H, alkyl, alkoxy, cycloalkyl, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl, aryloxy, polyether, cyano, nitro, halogen, trifluoromethyl, $-C(O)R^c$, $-(R^d)C(O)R^c$, $-CHO$, $(R^d)CHO$, $-COOR^c$, $-(R^d)COOR^c$, $-COO^-M^+$, $-(R^d)COO^-M^+$, $-SO_3R^c$, $-(R^d)SO_3R^c$, $-SO_3^-M^+$, $-(R^d)SO_3^-M^+$, $-SR^c$, $-(R^d)SR^c$, $-SOR^c$, $-R^d(SOR^c)$, $-NR^c$, $-(R^d)NR^c$, $-N^+(R^c)(R^c)(X^-)$ or $-(R^d)N^+(R^c)(R^c)(X^-)$, wherein

(e) R^c and R^d are the same or different, and are each H, or a branched or straight chain alkyl, alkoxy, cycloalkyl, polyether, cycloalkoxy, heterocycloalkyl, aryl, heteroaryl or aryloxy radical;

(f) M^+ is a cation; or

(vi) A is a bridging unit and is '-Ar-', which is an aryl or hereroaryl group of between 4 and 18 carbon atoms.

25. A process according to any one of Claims 1 to 24 inclusive, wherein the reaction temperature is from 50°C to 150°C; the synthesis gas pressure under which the hydroformylation reaction is performed is from 1 to 100 bar; and the H_2:CO ratio is from 1:10 to 100:1.